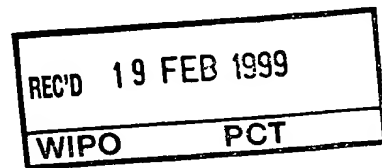




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PTY. LTD. filed on 19 January 1998.



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Patents Act 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"Process for Increasing the Melt Strength of Polypropylene (1)"

The invention is described in the following statement:

PROCESS

FOR INCREASING THE MELT STRENGTH OF POLYPROPYLENE

(1)

The present invention relates to polypropylene homopolymers and copolymers. In particular,
10 the present invention relates to a process for increasing the melt strength and/or the extensional
melt viscosity of said polymers by melt phase processing.

The melt strength and extensional viscosity of linear or straight chain polymers, such as
polypropylene, decreases rapidly with temperature. By contrast, polymers such as low density
15 polyethylene which are highly branched retain relatively high melt strengths and extensional
viscosities. It is generally understood that the difference in melt strengths and extensional
viscosities is attributable to the presence of long chain branching in polymers such as low
density polyethylene. Long chain branching allows a greater degree of chain entanglement.

20 A number of methods for increasing the melt strength/extensional viscosity of polypropylene
and related polymers through the introduction of branching or a limited degree of crosslinking
in a process involving reactive extrusion have been proposed and are summarised in a recent
paper by Wang et al. (Wang, X., Tzoganakis, C., and Rempel, G.L., *J. Appl. Polym. Sci.*,
1996, 61, 1395). One such process involves the reactive extrusion of polypropylene with a
25 polyfunctional monomer/initiator combination. For example, the use of pentaerythritol
triacrylate in combination with 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (DHBP).

White (US 5578682) has disclosed the use of various polyunsaturated crosslinking agents (for
example, bismaleimide derivatives) in combination with free radical initiators to achieve an
30 increase in the melt strength of various polymers.

It is well known that the melt phase processing of polypropylene leads to mechanochemical
degradation. The processing of polypropylene in the presence of free radical initiators provides

an increased rate of degradation. This controlled degradation of polypropylene is used commercially for the production of controlled rheology resins having reduced polydispersity and reduced die swell (Lambla, M. in *Comprehensive Polymer Science*, Pergamon, New York 1992, vol Suppl. 1, p 619; Hogt, A.H., Meijer, J., Jelinic, J. in *Reactive Modifiers for*
5 *Polymers*, Al-Malaika, S. Ed., Chapman & Hall, London, 1996, p 84.). The degradation of polypropylene as described therein results in a lowering of melt strength.

The batch modification of polypropylene to produce crosslinked (insoluble) polypropylene by treatment with peroxides is described by Borsig et al. (Borsig, E., Fiedlerova, A., Lazar, M.
10 *J., Macromol. Sci, Chem.*, 1981, A16, 513). Initiators which produce benzoyloxy radicals or phenyl radicals are described as being more efficient in inducing crosslinking or grafting than those which produce t-butoxy or alkyl radicals. The process requires the use of high levels of peroxide is described in Chodak, I.; Fabianova, K.; Borsig, E.; Lazar, M. *Agnew. Makromol. Chem.*, 1978, 69, 107. The use of polyfunctional monomers as coagents to retard
15 degradation and enhance crosslinking is also described. This work described is not predictive of the conditions required to achieve a gel-free, high melt strength material by continuous melt phase processing.

DeNicola (EP 384331A2) has disclosed a means to produce a branched propylene polymer
20 material showing a nett increase in the weight average molecular weight by solid state modification of predominantly isotactic semi-crystalline linear polypropylene. The process described in EP384331A2 involves blending peroxides with short half lives (eg peroxy dicarbonates) with linear propylene polymer in a mixing vessel at temperatures from 23°C to 120°C in an inert atmosphere and continuing to mix for a period of time until the peroxide
25 decomposes and polymer fragmentation and branching occurs without significant gelation of the polymer. DeNicola states that at temperatures greater than 120°C no branching or melt strength enhancement is achieved.

U.S. 5,464,907 teaches that certain unsaturated peroxides may be used to induce grafting in

polypropylene and α -olefin copolymers. They report that use of other peroxides generally results in chain degradation.

We have found that, with appropriate choice of conditions, melt mixing of polypropylene
5 homopolymer or ethylene-polypropylene copolymer in the presence of dibenzoyl peroxide (BPO) provides increased melt strength, increased extensional viscosity, increased molecular weight and broadened molecular weight distribution.

According to the present invention there is provided a process for modifying a polypropylene
10 (co)polymer wherein said process comprises melt mixing the polypropylene (co)polymer in the presence of benzoyl peroxide in an effective amount to provide a desired increase in the melt strength of the polypropylene (co)polymer. Advantageously the desired increase in melt strength may be obtained without the associated production of gels.

15 Polymers suitable for use in the present invention include a wide variety of polypropylene homopolymers, copolymers and blends containing one or more polypropylene homopolymers and/or copolymers.

Suitable polypropylene homopolymers include isotactic polypropylene, atactic polypropylene,
20 syndiotactic polypropylene. Commercial isotactic polypropylene having a proportion of mesodyeds of greater than 90% is preferably used in the process of the present invention. Isotactic polypropylene is a semi-crystalline polymer having a number of properties which have made it one of the most widely used commercial polymers. These properties include heat resistance, stress cracking resistance, chemical resistance, toughness, and low manufacturing
25 costs. However, the melt strength of isotactic polypropylene as measured directly by extensional viscosity or use of a commercial melt strength tester or indirectly by more qualitative measures such as drop time or die swell ratio is relatively low. This relatively low melt strength limits the use of polypropylene in applications such as foam extrusion, thermoforming and film blowing. In order to use polypropylene in such applications it is

necessary to employ sophisticated processing equipment. The present invention now permits this already widely used commercial polymer to be used in an even wider range of applications.

- 5 Polypropylene copolymers include copolymers of propylene and other monomers with such other monomers being present in amounts of preferably up to 10%wt. A preferred comonomer is ethylene.

The present invention is also applicable to other linear α -olefins. It is preferable that any such
10 other linear α -olefins are present in the polymer to be modified in amounts in excess of 90%wt.

The amount of dibenzoyl peroxide used in the process of the present invention should be an effective amount to achieve the desired increase in melt strength. Melt strength is considered
15 in the art to be an indication of long-chain branching in polyolefins. It is preferable in the process of the present invention that long-chain branching predominates over crosslinking in the reaction between the benzoyl peroxide and the polypropylene (co)polymer. Crosslinking of the polypropylene (co)polymer may result in the formation of gels which disrupt the appearance of the polypropylene (co)polymer. In the process of the present invention it is
20 desirable to control the degree and distribution of crosslinking and keep the level of ~~crosslinking as uniform and as low as necessary to produce the desired effects.~~ The amount of crosslinking which occurs in the polypropylene (co)polymer is dependant upon the amount of benzoyl peroxide melt mixed with the polypropylene (co)polymer. The amount of crosslinking is also dependent upon the degree of mixing as any regions high in benzoyl peroxide
25 concentration will result in excessive localised crosslinking and the formation of gels. It is desirable that good distributive and dispersive mixing be employed to promote even distribution of the benzoyl peroxide in the polypropylene (co)polymer so as to minimise the variation in benzoyl peroxide concentration throughout the polypropylene (co)polymer and reduce the likelihood of the formation of gels.

Preferably the benzoyl peroxide will be present in the range of from 0.1 to 5% by weight of the polypropylene homopolymer or copolymer ((co)polymer). The more preferred range being from 0.15% to 2.0% by weight of the polypropylene (co)polymer and even more preferred 5 range being from 0.15 to 1.8% by weight of the polypropylene.

The benzoyl peroxide is preferably introduced into the polymer melt directly, either neat (as a powder or a liquid), dispersed or dissolved in a suitable medium (for example, dissolved in 2-butanone) or adsorbed on polymer pellets or powder which may be added as a masterbatch. It 10 is desirable that the benzoyl peroxide is rapidly mixed with the polymer melt at a rate in keeping with the half life of the benzoyl peroxide at the processing temperature of the polypropylene (co)polymer.

The dibenzoyl peroxide may be added alone or along with any other polymer, additive or 15 filler, so that the polymer melts and with the benzoyl peroxide as it is decomposing. When the benzoyl peroxide is fed to the main feed throat of the extruder it is preferred to have a barrel temperature which is relatively low in the region adjacent to the main feed throat and increasing towards the die to prevent premature decomposition of the dibenzoyl peroxide.

20 The processability and other properties of the product may be improved by a chain scission step following the initial polymer modification step. This may be carried out by

- a) adding one or more additional initiators with or subsequent to the first initiator addition.
- b) high shear mixing
- c) high temperatures
- 25 d) some combination of (a) - (c) above

This additional step enables the production of a polymer enables tailoring the properties of the product to meet the requirements of the desired application. For example, by this two stage process it is possible to produce materials with similar melt viscosity to the base polymer but a

substantially increased melt strength. Use of the single stage process generally provide both an increase in melt strength and an increase in melt viscosity (see examples)

The second initiator may be added to the polypropylene (co)polymer during the modification process either with or subsequent to the benzoyl peroxide addition. The second initiator is typically added to give chain scission of the polypropylene (co)polymer so as to decrease the melt viscosity and improve the processability of the modified polypropylene (co)polymer. The additional should be introduced to the polymer_melt after the first initiator or have a sufficiently long half-life relative to the first initiator such that its decomposition can be staged to occur after the initial polymer modification process. Typically a polypropylene (co)polymer modified in accordance with the present invention may have a MFI < 1 g/10 min. With use of the second initiator an MFI > 1 g/10 min may be achieved. The second initiator may be selected from the group consisting of 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (DHBP), dicumyl peroxide (DCP), t-butyl peroxybenzoate (TBPB), t-butyl peroxy-2-ethylhexanoate (TBEH), and dilauryl peroxide (DLP) or any other initiator which can result in the overall chain scission of the polypropylene (co)polymer during melt processing. While the improvement in processability through chain scission normally results in some decrease in the melt strength/extensional viscosity of the modified polypropylene (co)polymer, the melt strength/extensional viscosity may still be acceptable, and improved over the unmodified polypropylene (co)polymer.

It is possible to combine the process of the present invention with other processes of polymer modification [which do not substantially interfere with the improved properties afforded by the process of the present invention.] or with, for example, the addition of fillers, additives or stabilisers, or blending with other polymers.

In the process of the present invention the polypropylene (co)polymer is melt mixed in the presence of benzoyl peroxide. Melt mixing may be carried out by any convenient means capable of mixing the polypropylene (co)polymer at temperatures above the melting point of

the polypropylene (co)polymer.

Suitable apparatus for melt mixing the polypropylene (co)polymer include continuous and batch mixers. Suitable mixing equipment includes extruders such as single screw and twin
5 screw extruders, static mixers, cavity transfer mixers and combinations of two or more thereof. It is preferred that the melt mixing is conducted in either a co- or counter- rotating twin screw extruder.

The barrel set temperatures are preferably in the range 80-280°C. Typical melt temperatures
10 are in the range 170-290°C.

In order to optimise the melt strength/extensional viscosity, the preferred melt temperatures are in the range 160°C to 220°C. This range provides optimal properties whilst minimising the amount of chain scission which occurs during processing. However, in some cases it may
15 be desirable to use higher temperatures such as in the venting/discharge sections of single screw or twin screw extruder or to induce some chain scission in order to decrease the molecular weight of the modified polypropylene (co)polymer and improve the processability of the modified polypropylene (co)polymer.

20 Typically, the die temperatures are in the range 180-290°C.

Preferably the extrusion conditions are adjusted so that the polypropylene (co)polymer and peroxide mixture are conveyed as quickly as possible into the melting/mixing zone to maximise the melt phase reaction (eg for twin screw extruders - high throughput rates, higher
25 screw speeds under starve fed conditions). It is more preferred that the additives are added to and mixed with molten polypropylene (co)polymer to further enhance the melt phase reaction. Preferably residence times in the range of from 10 seconds to 5 minutes are selected depending upon the temperature profile, throughput rate and peroxide levels. More preferred residence times are in the range of from 15 seconds to 120 seconds.

Vacuum venting can be applied to remove volatile by-products and solvents.

While not wishing to be bound by theory, it is believed that the effectiveness of benzoyl
5 peroxide in the present invention is determined by a number of factors, including:

- (i) the rate and specificity of hydrogen abstraction of the benzoyloxy or the derived phenyl radicals. Benzoyloxy/phenyl radicals have less specificity for abstraction of tertiary vs. primary or secondary hydrogens than do, for example, alkoxy or alkyl radicals. The
10 rate of reaction of benzoyloxy and phenyl radicals is significantly higher than that of alkoxy or alkyl radicals.
- (ii) the initiator half-life. The use of conditions which result in a short initiator half-life will generate locally high concentrations of radicals thus increasing the likelihood of
15 radical combination events.
- (iii) the solubility characteristics of the peroxide in the polymer melt.

Other initiators that meet the above criteria may also be used to advantage in the present
20 invention.

Surprisingly, the process of the present invention results in a polypropylene (co)polymer with substantially increased melt strength. We have found that it is possible with the present invention to obtain a polypropylene (co)polymer which has a melt strength at least 25% greater
25 than the melt strength of the base polymer. We have also found that it is possible to obtain an increase in melt strength of greater than 100% for a number of the polypropylene (co)polymers produced in accordance with the process of the present invention. Increases in melt strength were assessed using a Gottfert-Rheotens melt strength tester operated with a roller acceleration of 1.2 cm/sec² measuring the melt strength of a 2 mm diameter strand of molten polypropylene

(co)polymer (melt temperature of 210°C) which is fed to the Gottfert tester at ~4 g/min.

In a further aspect of the present invention there is provided a modified polypropylene (co)polymer produced according to the process described herein, wherein said modified
5 polypropylene (co)polymer preferably has a melt strength at least 25%, and more preferably at least 100%, greater than the unmodified polypropylene (co)polymer.

The polypropylene (co)polymers produced according to the process of the present invention also may provide a significant increase in long-chain branching. Long-chain branching may be
10 assessed by the Dow Rheology Index. Advantageously, the modified polypropylene (co)polymers may demonstrate a Dow Rheology Index (DRI) of greater than 1, preferably at least 2 and most preferably greater than 50.

The process of the present invention may also be used to increase the melt elasticity of a
15 polypropylene (co)polymer.

Advantageously, the process of the present invention also provides a means to alter the molecular weight, molecular weight distribution and/or degree and length of branching of polypropylene, ethylene-propylene copolymers, and analogous α -olefin copolymers with or
20 without altering the melt strength of said polymers by melt processing.

The process of the present invention may provide a means to generally increase the molecular weight and broaden the molecular weight distribution and/or to introduce branching of the polypropylene (co)polymer. This will not always equate to significant increases in the melt
25 strength or extensional viscosity of the polymer that is being modified (eg modification of a lower mol. wt. polymer to broaden the mol. wt. and/or introduce shorter branches.) Such a product may not necessarily demonstrate a high melt strength, but may demonstrate other desirable properties, for example improved filler uptake, mechanical properties, thermal and morphological properties.

The modified polypropylene (co)polymer produced by the process of the present invention may be used either neat or blended with another polymer or other additives to provide the desired balance of properties in the polymer blend.

5

The modified polypropylene (co)polymers and blends may be used in a wide variety of applications including thermoforming, blowmoulding, tube or pipe extrusion, blown films, foams.

- 10 The present invention may also be used in the recycling of waste polypropylene or materials containing waste polypropylene.

The increased melt strength of the modified polypropylene (co)polymers renders these (co)polymers suitable for use in thermoforming applications. The modified polypropylene
15 (co)polymers may be used to thermoform containers such as margarine tubs. The benefits of this invention that the polypropylene (co)polymers and blends containing same provide a water processing window. The modified polypropylene (co)polymers may also be used in large part thermoforming such as in the production of refrigerator liners and the like where conventional isotactic polypropylene is unsuitable.

20

The modified polypropylene (co)polymers produced in accordance with the present invention are suitable for blow moulding and we have found that they can be more readily blow moulded into containers. Furthermore, the increased melt strength makes it possible to produce large blow moulded parts through the use of the high melt strength modified polypropylene
25 (co)polymer. Thus components currently made by rotational moulding may now be produced by blow moulding using the modified polypropylene (co)polymer of the present invention.

Profile extrusion tube and pipe extrusion, of the modified polypropylene (co)polymer has been found to produce a more consistent product and the polypropylene (co)polymer of the present

invention may be advantageously used in this type of extrusion application.

Blown films made of polypropylene are generally blown downwards using relatively expensive equipment. The modified polypropylene (co)polymers of the present invention have sufficient
5 melt strength to be able to be blown upwardly using conventional polyethylene type film blowing equipment which is less expensive and generally more convenient to operate. Advantageously the modified polypropylene (co)polymers of the present invention may be used in the production of blown films.

10 The modified polypropylene (co)polymers of the present invention may also be foamed (either using physical or chemical blowing agents), such as the use of carbon dioxide as a physical blowing agent to produce foams having a fine closed cell structure with a wider processing window then for conventional polypropylene. Foamed pellets may be subsequently moulded to form components for use in a variety of applications such as automotive door trims,
15 rooflinings, dash boards, bumpers and the like. Applications such as in packaging are also possible, including thermoformed containers, insulating cups and the like.

Waste polypropylene and waste streams containing a significant proportion are presently difficult to recycle as conventionally a high degree of chain scission results from the recycling
20 process. The process of the present invention may be used to upgrade recycled streams containing polypropylene by increasing the overall mechanical properties of the recycled polypropylene by the addition of benzoyl peroxide in accordance with the present invention.

The present invention will now be described with reference to the following non-limiting
25 examples. Described hereunder are the measurement techniques used in the examples and a full description of the process conditions employed. Comparative Examples are labelled CE-n.

Melt Strength Measurement

Melt strengths were measured on a "Rheotens" Melt Strength Tester, Type 010.1, supplied by Gottfert Werkstoff-Prufmaschinen GmbH of Buchen, Germany. This test involves drawing an
5 extruded strand of polymer vertically into the nip between two counter-rotating nip rollers. The strand was extended using a Brabender Plasticord single screw extruder of screw diameter 19mm and length to diameter ratio (L/D) of 25. The extrudate exited via a right angle capillary die (2mm diameter). The temperature profile used was uniform along the length of the barrel of the extruder and the die and was set at 190°C. The nip rollers are mounted on a
10 balance arm which allows the force in the drawing strand to be measured. The velocity of the nip rolls is increased at a uniform acceleration rate. As the test proceeds, the force increases until eventually the strand breaks. The force at breakage is termed the "melt strength".

While there is no internationally-established standard set of test requirements for melt strength
15 testing, comparative melt strength values obtained under the given set of test conditions provide a quantitative determination of the increase in melt strength used in the patent. The test conditions used were: die temperature 190°C, extruder output rate ~4 g/min, acceleration rate 1.2 cm/sec², draw distance 210 mm, on matt finish steel rollers.

20 Dow Rheology Index

The Dow Rheology Index (DRI) is believed in the art to be a measure of the long chain branching in a polymer. It is expressed as the deviation of a viscosity parameter obtained from shear rheology measurements on a "branched" polymer compared with that for a linear
25 polymer. The branched polymers have lower values of the viscosity parameter than the linear polymers (for a given relaxation parameter). The parameters are obtained by fitting the Cross model to the shear viscosity flow curves. The DRI method has been described by Lai, Plumley, Butler, Knight and Kao in a paper in SPE ANTEC '94 Conference Proceedings (pp1814-1818) - "Dow Rheology Index (DRI) for Insite Technology Polyolefins (ITP): Unique

Structure-Processing Relationships"

Dynamic Rheology Tests

- 5 The dynamic rheology tests were performed on a Rheometrics Dynamic Stress Rheometer SR200. Test conditions were: parallel plates, temperature 190°C, frequency range 0.01 to 100 rad/sec, and 3-4% strain, in a nitrogen atmosphere to prevent degradation. G' is the storage modulus representing the elasticity of the polymer melt, G'' is the loss modulus which represents the viscous component of the deformation. The polydispersity index is 10 to power 10 5 divided by the crossover modulus, which is the value of $G' = G''$ when the G' and G'' curves crossover - it is believed to be a measure of MWD. The higher G' , the greater elasticity in the polymer and the higher the MW.

MFI

15

Melt flow indexes (MFI) were measured at 230°C with a 2.16 kg load according to ASTM 1238.

Drop Times

20

- The drop times were determined by measuring the time taken for the polypropylene strand (cut at the die face) to drop from the die of the extruder to the floor. The die of the JSW twin screw extruder was 1140 mm above the floor. The drop time test combines the effects of melt viscosity, extensional viscosity, chain entanglement (as shown by die swell), and elasticity (as 25 shown by the tendency resist neck formation). Higher melt viscosity polypropylene polymers had drop times which incorporated some additional effect due to prolonged cooling of the slower moving (falling) molten strand.

GPC

Molecular weights were determined by gel permeation chromatography on a linear Ultrastyrigel column using 1,2,4-trichlorobenzene at 140°C as the eluent. Calibration was
5 performed using monodisperse polystyrene standards.

Twin Screw Extruder

The twin screw extruder used in the examples was a JSW TEX-30 with a 30 mm screw
10 diameter and an overall L/D of 42 [comprising ten temperature controlled barrel sections (L/D
3.5, temperatures between 120 and 230°C as specified in Table 1), three unheated
sampling/monitoring blocks (L/D 1.167) and a cooled feed block (L/D 3.5)) equipped with
two JSW TTF20 gravimetric feeders, one K-Tron KQx gravimetric additives feeder and a
volumetric liquid addition pump (Fuji Techno Industries model HYM-03-08)]. The extruder
15 was operated in either co-rotating (intermeshing self wiping) or counter rotating (intermeshing
non-self wiping) modes with a throughput rate of between 5 and 20 kg/hr and screw speed of
between 100 and 400 rpm as specified in Table 1. The melt temperature and pressures were
monitored at three points along the barrel and in the die.

Table 1 Operating conditions

Conditions	Screw Speed (rpm)	Feed Rate (kg/hr)	Temperature Profile (°C)
A	265	20	150°C, 175°C (by 10)
B	265	20	180°C, 200°C (by 3), 220°C (by 7)
C	150	5	120°C, 130°C (by 4), 180°C (by 6)
D	265	20	140°C, 150°C (by 10)
E	265	20	180°C, 200°C (by 4), 230°C, 240°C, 250°C, 260°C, 270°C, 280°C.
F	400	20	180°C, 220°C (by 10)
G	265	20	80°C, 120°C, 140°C, 160°C, 170°C, 180°C, 200°C (by 5)
H	150	5	80°C, 120°C, 140°C, 160°C, 170°C, 180°C, 190°C (by 3), 200°C (by 2)
I	265	20	80°C, 120°C, 140°C, 160°C, 170°C, 180°C, 190°C (by 3), 200°C (by 2)

- The temperatures in the table refer to sections of the barrel of the extruder that are capable of independent temperature control. The first ten temperatures are barrel section temperatures and the last temperature indicates the temperature of the die.

Table 2 - JSW die configuration - for drop times

Condition	Die Description
1	Large 3 hole strand die - 6 mm holes
2	Small 3 hole strand die - 4 mm holes
3	Large 2 hole strand die - 6 mm holes
4	Single hole Brabender die- 10mm hole

Table 3 - Means of modifier addition

Condition	Die Description
α	Modifier added at block 4 in 2-butanone carrier solvent
β	Modifier added at block 4 in xylene carrier solvent
γ	Modifier coated onto PP powder - pre tumble blended
δ	Modifier coated onto PP powder masterbatch

5 The overall extruder configuration may be recited, for example, as follows: A1 δ .

Solvent Addition of Modifiers

The benzoyl peroxide was used as a powder wetted with 25 wt% water. The benzoyl peroxide
10 was introduced as a solution in 2-butanone or xylene. The concentration of the benzoyl peroxide varied from 5.6% wt/wt to 8.5% wt/wt.

Increased levels of benzoyl peroxide were generally added by increasing the amount of solution added to the polymer melt. The second peroxide (if used) was added with benzoyl
15 peroxide in the carrier solvent.

Solid Addition of Modifiers

For the solventless modification of the polymer the benzoyl peroxide was generally absorbed onto or blended with powdered polymer at concentrations ranging from 5% wt/wt to 10% wt/wt to form a masterbatch. The masterbatch was added to the extruder in varying feed rates to alter the amount of additives. The amount of polymer feed was adjusted accordingly to give constant overall feed rate.

The stabilisers were also added as a masterbatch. The amount of stabiliser was generally kept constant at 0.33wt% Irganox 1010 and 0.17wt% Irgaphos 168 in the total composition.

The main polymer feed was added as either powder or pellets.

Single Screw Extruder

15

The single screw extruder used in the examples was a Killion segmented single screw extruder of L/D=40 (11 barrel sections , 10 heated) and screw diameter of 31.75 mm.

Polypropylene powder, stabilisers (0.33wt% Irganox 1010, 0.17wt% Irgaphos 168 in total) and benzoyl peroxide were added to the feed throat of the single screw extruder via a twin screw K-Tron volumetric feeder.

Alternatively, the polypropylene powder and stabilisers were added via the K-Tron feeder and polypropylene powder, stabilisers and the modifiers were added as a master batch via a single screw APV Accurate volumetric feeder. The masterbatch contained 7.5wt% benzoyl peroxide (prepared using a dispersion of benzoyl peroxide containing 25wt% water).

The output of the extruder was ~1.5 kg/hr using a screw speed of 30rpm. The set barrel temperature was either (i) a flat 220°C with each barrel section and the die set at a temperature

of 220°C or (ii) 230°C/190°C with the first six melting sections of the barrel set at 230°C and the next four metering sections of the barrel and the die set at 190°C. The melt temperature varied from 220 to 260°C.

- 5 The following commercial polypropylene (co)polymers were used in the examples. The properties of the (co)polymers are shown in Table 4 below.

Table 4: Comparative data for a grade of high melt strength PP and conventional PP grades.

Example	Polymer	Polymer Description	MFI 2.16kg @ 230°C	Melt Strength cN
Control 1	Montell PF814	High melt strength polypropylene homopolymer	3	18
Control 2	Montell JE6100	Extrusion grade polypropylene homopolymer	3	3
Control 3	ICI Australia GYM 45	Injection moulding grade of polypropylene homopolymer	14	1.8
Control 4	ICI Australia GWM 22	Extrusion grade of polypropylene homopolymer	4	2.8
Control 5	ICI Australia PXCA 6152	Thermoforming grade of polypropylene homopolymer	0.8	6
Control 6	ICI Australia LYM 120	Injection moulding grade of propylene/ethylene copolymer	14	1.4
Control 7	Montell 6501	Ex-reactor grade of injection moulding polypropylene homopolymer	4.1	~3

Examples 1 to 4

GYM45 was modified in accordance with Table 5 below. GYM45 is a low molecular weight/higher MFI injection moulding grade of polypropylene homopolymer.

5

Table 5: Effect of addition of BPO in 2-butanone upon modification of GYM45.

Example	Conditions	BPO (wt%)	Motor Current (amps)	Die Temp. (°C)	Drop Time (secs.)	MFI 2.16kg @ 230°C	Melt Strength (cN)
Control 3	-	-	-	-	-	14	1.8
CE 1	B1α	0	13	231	8	12.2	1.5
1	B1α	0.36	13	229	9.7	14.4	1.9
2	B1α	0.7	13	229	13.5	14.4	2.3
3	B1α	0.95	13	230	17.1	12.5	3
4	D3α	1.0	19	197	23	9.7	4

Examples 1 to 3 show an increase in the melt strength corresponding to an increase in BPO.

The melt strength of example 3 is approximately twice that of the controls. A comparison of 10 examples 3 and 4 shows an increase in melt strength and decrease in MFI with a decrease in barrel set temperature.

Examples 5 to 8

15 GWM22 was modified in accordance with Table 6. GWM22 is an intermediate molecular weight/medium MFI extrusion grade of polypropylene homopolymer.

Table 6: Effect of addition of BPO in 2-butanone upon the modification of GWM22

Example	Conditions	BPO (wt%)	Motor Current (amps)	Die Temp. (°C)	Drop Time (secs.)	MFI 2.16kg @ 230°C	Melt Strength (cN)
Control 4	-	-	-	-	-	4.5	2.8
CE 2	B1α	0	16	239	11.3	5	-
5	B1α	0.36	16	234	15.2	6.3	3
6	B1α	0.75	17	238	21.8	5.9	4.7
7	B1α	1	16	239	25.4	5	6.9
8	B1α	1.3	20	236	25.3	5.6	7.1

5 Examples 5 to 8 show an increase in the melt strength with an increase in BPO. There is also generally an increase in the drop time.

The melt strength of GWM22 more than double as a result of the addition of 1 wt% BPO.

Examples 9 to 12

10

PXCA6152 was modified in accordance with Table 7 below PXCA6152 is a high molecular weight/low MFI thermoforming grade of polypropylene homopolymer.

Table 7: Effect of addition of BPO in 2-butanone upon the modification of PXCA6152

Example	Conditions	BPO (wt%)	Motor Current (amps)	Die Temp. (°C)	Drop Time (secs.)	MFI 2.16kg @ 230°C	Melt Strength (cN)
Control 5	-	-	-	-	-	0.8	6
CE3	B1 α	0	-	245	-	0.84	5.9
9	B1 α	0.34	22	244	25.9	1.3	7.4
10	B1 α	0.68	23	250	22.8	1.1	11.1
11	B1 α	0.8	24	246	30.5	0.8	14
12	B1 α	1.04	24	247	25.3	0.65	17.7

Examples 9 to 12 show a significant increase in the melt strength with an increase in the level 5 of BPO. The melt strength approximately trebled as a result of the addition of 1 wt% BPO.

The modified polypropylene of example 12 was tested for additional physical properties and it was found that the modified polypropylene had:

10	i)	Elasticity	200	G' @0.01 rad/s (Pa)
	ii)	1/Relaxation Time	7.1	Crossover frequency (rad/sec)
	iii)	Polydispersity Index	3.9	M _w /M _n
	iv)	Dow Rheology Index	10	Long Chain Branching

15 The DRI of the base polypropylene material, PXCA 6152 (an unbranched polypropylene) was expected to be 0. The DRI of the modified polypropylene demonstrates a significant degree of long chain branching

Examples 13 and 14

LYM120 was modified in accordance with Table 8 below. LYM120 is a low molecular weight/higher MFI injection moulding grade of PP copolymer.

Table 8: Effect of addition of BPO in 2-butanone upon the modification of LYM120.

Example	Conditions	BPO (wt%)	Motor Current (amps)	Die Temp. (°C)	Drop Time (secs.)	MFI 2.16kg @ 230°C	Melt Strength (cN)
Control 6	-	-	-	-	-	12.2	1.4
13	D2 α	0.68	13	182	19.3	13.1	2.3
14	A4 α	1.08	19.5	200	31	9	4.2

10 Examples 13 and 14 show an increase in the melt strength with the addition of BPO.

Examples 15 to 20

Ex-reactor GYM45 powder was modified according to Table 9 below. GYM45 is a low molecular weight/higher MFI injection moulding grade of polypropylene homopolymer.

Table 9: Effect of a feed throat addition of BPO and stabilisers to ex-reactor GYM45 powder.

Example	Conditions	BPO (wt%)	Motor Current (amps)	Die Temp. (°C)	Drop Time (secs.)	MFI 2.16kg @ 230°C	Melt Strength (cN)
Control 3						14	1.8
CE 4	H38	0	7	209	21.5	11.3	1.7
15	I38	0.38	14	209	12.1	13.6	1.9
16	I38	0.75	15	210	15.0	11.8	2.6
17	I38	1.5	15	214	20.6	10.3	5.7
18	H38	0.75	6	209	35.5	17.6	2.1
19	H38	1.13	8	208	39.5	13.3	2.9
20	H38	1.5	8	208	43.3	9.8	4.4

Examples 15 to 20 show that under set conditions the melt strength (and drop time) of GYM45 PP ex-reactor powder increases with the addition of increasing levels of BPO.

Examples 21 to 23

LYM120 was modified in accordance with Table 10 below. LYM120 is a low molecular weight/higher MFI injection moulding grade of polypropylene copolymer.

Table 10: Effect of feed throat addition of BPO and stabilisers to ex-reactor LYM120 powder.

Example	Conditions	BPO (wt%)	Motor Current (amps)	Die Temp (°C)	Drop Time (secs.)	MFI 2.16kg @ 230°C	Melt Strength (cN)
Control 6						12.2	1.4
CE 5	H38	0	7	209	18.4	11.3	1.2
21	H38	0.75	8	210	50.5	6.9	2.6
22	H38	1.13	8	210	47.0	6.6	3.3
23	I38	1.5	14	217	18.5	3.8	6.1

Examples 21 to 23 show that the melt strength of GYM45 PP ex-reactor powder increases with the addition of increasing levels of BPO.

Examples 21 to 23 also show a decrease in the MFI with increasing levels of BPO.

Examples 24 to 28

10 LYM120 was modified in accordance with Table 11 below. LYM120 is a low molecular weight/higher MFI injection moulding grade of polypropylene copolymer.

Table 11: Effect of feed throat addition of BPO and stabilisers to ex-reactor LYM120 powder.

Example	Conditions	Initiator	Initiator (wt %)	Motor Current (amps)	Die Temp. (°C)	Drop Time (secs)	MFI 2.16kg @ 230°C	Melt Strength (cN)
CE-6	A3	-	0	14.5	200	10	12.4	1.1
24	A3	BPO	0.11	14	199	10	11.5	1.1
25	A3	BPO	0.23	16.5	201	15.1	9.0	1.2
26	A3	BPO	0.45	16.5	203	20.6	6.6	1.7
27	A3	BPO	0.68	17.5	206	20.6	5.4	4.1
28	A3	BPO	1.13	18	206	18.6	5.7	3.9
CE-7	A3	DLP	0.31	13.5	198	9.3	13.6	-
CE-8	A3	DLP	0.59	14	199	8.8	14.4	-
CE-9	A3	DLP	0.89	13	196	8.9	15.0	-
CE-10	A3	TBPB	0.07	12	189	5.1	28.7	-
CE-11	A3	TBPB	0.15	12	190	5.3	31.0	-
CE-12	A3	TBPB	0.29	10.5	185	6.3	92.0	0.5
CE-13	A3	TBPB	0.59	11	186	11.2	102.0	-

Examples 29 to 32

5 GYM45 was modified in accordance with Table 12 below. GYM45 is a low molecular weight/higher MFI injection moulding grade of polypropylene homopolymer.

Table 12 Effect of addition of different peroxides in 2-butanone upon the modification of GYM 45.

Example	Conditions	Initiator	Initiator (wt%)	Motor Current (amps)	Die Temp. (°C)	Drop Time (secs)	MFI 2.16kg @ 230°C
CE 14	A3α	-	0	18	192	11.8	12.8
29	A3α	BPO	0.23	16.5	196	10.35	17.0
30	A3α	BPO	0.45	17	199	11.8	17.3
31	A3α	BPO	0.73	17	200	15.9	15.4
32	A3α	BPO	0.96	18	202	17.3	14.9
CE-15	A3α	DHBP	0.08	15	191	3.6	96
CE-16	A3α	DHBP	0.17	14.5	190	3.1	169
CE-17	A3α	DHBP	0.29	13	188	2.3	>100
CE-18	A3α	DHBP	0.30	13	188	2.2	>200
CE -19	A3α	DHBP	0.50	13.5	186	1.9	>200
CE-20	A3α	DHBP	0.57	12	186	1.9	>100
CE-21	A3α	TBEH	0.30	17	197	8.8	12.0
CE-22	A3α	TBEH	0.64	14	188	7.2	24.4
CE-23	A3α	TBEH	0.98	14	189	6.8	25.6
CE-24	A3α	TBPB	0.31	13	186	2.6	95
CE-25	A3α	TBPB	0.64	13	184	2.1	238
CE-26	A3α	TBPB	1.03	12	184	1.9	>250
CE-27	A3α	DCP	0.08	16	192	3.8	47.1
CE-28	A3α	DCP	0.17	14	189	2.9	121.3
CE-29	A3α	DLP	0.32	16	191	10.9	14.5
CE-30	A3α	DLP	0.64	16	190	10.6	17.9
CE-31	A3α	DLP	0.95	16	189	10.4	16.6

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Examples 29 to 32 show an increase in drop time and decrease in MFI with increasing level of BPO, whereas for the other peroxides the drop time decreases and the MFI increases with increasing peroxide. The high MFI values indicate a very high degree of chain scission

Examples 33 to 37

LYM120 was modified in accordance with Table 13 below. LYM120 is a low molecular weight/higher MFI injection moulding grade of polypropylene copolymer.

Table 13: Effect of addition of different peroxides in 2-butanone upon the modification of LYM120.

Example	Conditions	Initiator	Initiator (wt%)	Motor Current (amps)	Die Temp. (°C)	Drop Time (secs)	MFI 2.16kg @ 230°C
Control 24	A3 α	BPO	0	16	195	9.9	12.8
33	A3 α	BPO	0.25	15	196	10.3	13.4
34	A3 α	BPO	0.47	14	198	13.2	13.1
35	A3 α	BPO	0.64	16	198	13.9	12.9
36	A3 α	BPO	0.70	17	201	13.6	11.9
37	A3 α	BPO	0.94	18	198	13.5	10.6
CE-32	A3 α	DHBP	0.09	14	190	3.6	80
CE-33	A3 α	DHBP	0.16	13	188	3.1	160
CE -34	A3 α	DHBP	0.26	13	187	2.8	250
CE-35	A3 α	TBEH	0.29	15	193	7	
CE-36	A3 α	TBEH	0.60	13	192	6.7	19.4
CE-37	A3 α	TBEH	1.02	12	191	6	22.6
CE-38	A3 α	TBPB	0.30	13	186	3.6	85
CE-39	A3 α	TBPB	0.61	12	184	3.8	173
CE-40	A3 α	TBPB	0.92	12	184	3.4	> 250
CE-41	A3 α	DCP	0.08	16	192	4.5	14.6
CE-42	A3 α	DCP	0.17	13	190	3	107
CE-43	A3 α	DCP	0.25	13	188	3	131
CE-44	A3 α	DLP	0.32	14.5	191	9.5	14.3
CE-45	A3 α	DLP	0.68	15	191	9.4	15.8
CE-46	A3 α	DLP	0.98	14.5	193	8.7	21.0

Examples 33 to 37 show an increase in drop time with increasing level of BPO, indication an increase in melt strength, whereas the other peroxides show a decrease in drop time and an increase in MFI with increasing peroxide. The high MFI values indicate a very high degree of chain scission.

Examples 38 and 39

Montell 6501 was modified in accordance with Table 14 below on the Killion SSE described above.

Table 14: Effect of feed throat addition of BPO and stabilisers to Montell 6501 ex-reactor powder.

Sample	Barrel Temp. (°C)	Extruder Output (kg/hr)	BPO wt %	Motor Current (amps)	Die Temp. (°C)	Drop Time (secs.)	MFI (g/10 min.)
Control 7	-	-	-	-	-	-	4.1
CE 47	220 flat	1.4	0	6	256	17	4.1
38	230/190	1.5	0.86	5	222	33.0	5.5
39	230/190	1.7	1.70	-	-	-	2.2

Example 33 shows an increase in the drop time with the addition of BPO which is indicative of an increase in the melt strength of the Montell 6501. Example 34 shows a decrease in the MFI which has also been shown to be indicative of an increase in the melt strength of the polymer.

Examples 40, 41, 7, 12, 28, 29, 31 and 14

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GPC molecular weights were determined using a Waters 150C high temperature GPC unit.

1,2,4-trichlorobenzene was used as the solvent, eluting through two Ultrastyrigel linear columns. The oven temperature was set at 140°C and the pump flow rate was 1.0ml/min.

Calibration was performed using narrow polydispersity polystyrene standards. All molecular weights quoted as linear polystyrene equivalents.

Mn = number average molecular weight

Mw = weight average molecular weight

Mz = viscosity average molecular weight

Mp = peak molecular weight

10 Error are quoted as two times the standard deviation between duplicate injections.

Table 15: GPC molecular weights for various modified PPs.

Example No.	Cond.	BPO (wt%)	MFI (g/10 min)	Melt Str. (cN)	Mn	Mw	Mz	Mp
Intermediate Molecular Weight PP Homopolymer(GWM 22)								
Control 4	-	-	4	2.8	55	295	1200	105
40	C2 α	1.50	3.8	-	75	430	1560	160
41	C2 α	2.23	3.2	-	75	430	1700	150
7	B1 α	1.0	5.0	6.9	80	425	1415	200
High Molecular Weight PP Homopolymer (PXCA 6152)								
Control 5	-	-	0.84	6	245	695	1500	635
CE 3	B1 α	0	-	-	160	580	1500	330
12	B1 α	1.04	0.65	17.7	110	485	1615	195
Low Molecular Weight- PP Copolymer (LYM 120)								
Control 6	-	-	12.4	1.4	45	230	720	130
33	A3 α	0.25	13.4	-	70	315	1330	135
34	A3 α	0.47	13.1	-	65	320	1380	130
36	A3 α	0.64	12.9	-	65	360	1975	130
14	D2 α	0.68	13.1	2.3	70	445	1865	140

*Errors in molecular weight are generally less than 30% of the quoted value, as is usual in high temperature GPC under the conditions employed.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and
5 scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

DATED this 19th Day of January, 1998

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